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(54) Catalytic system for the (co)polymerization of alpha-olefins

(57) A catalytic system with an increased activity for the (co)polymerization of alpha-olefins comprises a catalyst of the metallocene type, which is capable of polymerizing olefins without aluminoxane, and a weak co-ordinating polar compound.

The polymerization process based on this catalytic system enables a higher productivity to be obtained with respect to an analogous process carried out with the metallocene-type catalyst as such.

European patent application pub. No. 648,786 relates to a polymerization catalyst comprising an ionic metallocene and a Lewis base. Although increased polymerization activities are shown at high temperature with diisobutylphthalate, the strong Lewis bases disclosed in this reference are known to have a poisoning effect on olefin polymerization catalyst which make their use unsuitable for many processes at low to medium temperature.

The demand for metallocene catalysts with a high activity excluding the use of aluminoxanes as activators therefore remains unanswered.

The Applicant has now surprisingly found that the activity of metallocene catalysts not comprising aluminoxanes is considerably increased in the presence of particular organic substances not containing metals.

A first object of the present invention therefore relates to an improved catalyst for the (co)polymerization of alpha-olefins comprising the following components in contact with each other:

(A) a metallocene derivative of a metal selected from the group consisting of transition metals and lanthanides, capable in itself of promoting the polymerization of olefins without organo-oxygenated compounds of metals of groups 13 or 14 of the periodic table of elements,

(B) a substance not containing metal atoms, characterized in that this substance (B) consists of an aprotic polar compound having a weak co-ordinating capacity.

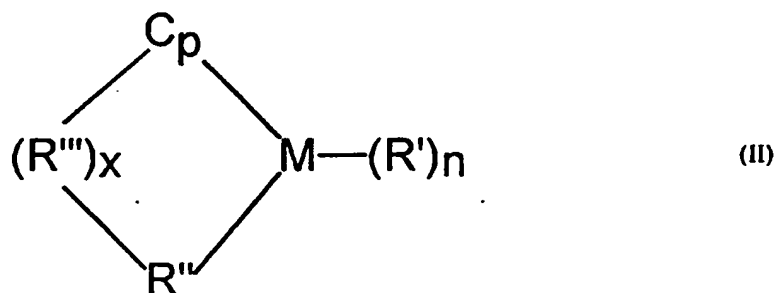
A second object of the present invention relates to an improved process for the (co)polymerization of alpha-olefins characterized in that it is carried out in the presence of the above improved catalyst.

The term "(co)polymerization of alpha-olefins" as used hereafter in the text and claims refers both to the homopolymerization and copolymerization of alpha-olefins with each other or with another ethylenically unsaturated polymerizable compound.

The metallocene derivative (A) of the present invention is an organometallic compound of a transition metal or lanthanide, preferably a metal selected from Ti, Zr and Hf, characterized by the presence of at least one  $\eta^5$ -cyclopentadienyl group co-ordinated to the metal, and by the capacity of promoting the polymerization of alpha-olefins also without an organo-oxygenated compound of a metal of groups 13 or 14 of the periodic table. These organo-oxygenated compounds are monomeric or polymeric organometallic derivatives containing at least one oxygen atom linked to a metal of group 13 or 14 of the periodic table, such as, for example, aluminoxanes, especially methylaluminoxane, galloxanes or stannoxanes, which are widely used as co-catalysts of many catalytic systems based on metallocenes.

The elements silicon and carbon, belonging to group 14 of the periodic table of elements are not considered metals for the purposes of the present invention. In accordance with the present invention the term "transition metals" refers to metals of groups 3 to 10 of the periodic table, whereas "lanthanides" are metals having an atomic number of between 57 and 71.

Metallocene derivatives (A) of the type defined above are known and have been widely described in literature. They usually consist of an ionic (anion-cation) system in which the cation comprises the metallocene. These metallocene derivatives (A) can be obtained by different methods described in literature, generally by the reaction of a metallocene with a compound capable of extracting a group sigma-bonded to the metal with the formation of a cationic species. Metallocenes which are suitable for the formation of these ionic metallocene derivatives are those having the following general formula (II):



wherein:

M represents a metal selected from metals of groups 3 to 5, or from the group of lanthanides in the periodic table of elements;

Cp is an anion containing a  $\eta^5$ -cyclopentadienyl ring co-ordinated to the metal M,

each of the n R' independently represent a substituent group selected from hydride, halide, a C<sub>1</sub>-C<sub>8</sub> alkyl group, a

linear or branched, or a mixture thereof, X is a halogen, preferably chlorine or bromine, and "m" is a decimal number comprised between 1 and 3;

Metallocene catalysts active in the polymerization of olefins without aluminoxane, which are suitable as component (A) of the catalyst of the present invention are described, for example, in the publications mentioned above relating to cationic metallocene derivatives of the known art, as well as in the following patent publications, whose contents are herein incorporated as reference:

- European patent application published with the Nr.: EP-A 522.581, EP-A 495 375, EP-A 520732, EP-A 478913, EP-A 468651, EP-A 427697, EP-A 421659, EP-A 418044;
- International patent applications published with the Nr.: WO 92/00333, WO 92/05208;
- U.S. patents 5064802, 2827446, 5066739.

Non-limiting examples of metallocene derivatives (A) which can be used for the formation of the catalyst of the present invention are listed below in table 1, with reference to the respective precursors from whose combination they are obtained. Accordingly, each metallocene compound in the left column can be combined with each ionizing compound in the right column.

TABLE 1

Metallocene	Co-catalyst (C)
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl <sub>2</sub>	AlEtCl <sub>2</sub>
( $\eta^5$ -THInd) <sub>2</sub> ZrCl <sub>2</sub>	AlR <sup>6</sup> <sub>3</sub> + B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ZrCl <sub>2</sub>	AlR <sup>6</sup> <sub>3</sub> + [Ph <sub>3</sub> C] <sup>+</sup> · [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>
[1,2-en( $\eta^5$ -Ind) <sub>2</sub> ]ZrCl <sub>2</sub>	AlR <sup>6</sup> <sub>3</sub> + [Bu <sup>n</sup> <sub>3</sub> NH] <sup>+</sup> · [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>
( $\eta^5$ -Ind)Zr(NMe <sub>2</sub> ) <sub>3</sub>	AlR <sup>6</sup> <sub>3</sub> + [PhNMe <sub>2</sub> H] <sup>+</sup> · [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>
[Ph <sub>2</sub> Si( $\eta^5$ -Ind) <sub>2</sub> ]ZrCl <sub>2</sub>	AlR <sup>6</sup> <sub>3</sub> + [Li] <sup>+</sup> · [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>
[Me <sub>2</sub> Si( $\eta^5$ -Ind) <sub>2</sub> ]HfCl <sub>2</sub>	AlR <sup>6</sup> <sub>3</sub> + [Li] <sup>+</sup> · [Al(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>
[Pr( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )( $\eta^5$ -Flu)]ZrCl <sub>2</sub>	AlR <sup>6</sup> <sub>3</sub> + [PhNMe <sub>2</sub> H] <sup>+</sup> · [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>
[Me <sub>2</sub> Si( $\eta^5$ -C <sub>5</sub> Me <sub>4</sub> )(NBu <sup>t</sup> )]TiCl <sub>2</sub>	
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ZrCl(NMe <sub>2</sub> )	
( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> ZrMe <sub>2</sub>	[Ph <sub>3</sub> C] <sup>+</sup> · [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiClMe	[Bu <sup>n</sup> <sub>3</sub> NH] <sup>+</sup> · [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>
[1,2-en( $\eta^5$ -THInd) <sub>2</sub> ]ZrMe <sub>2</sub>	[PhNMe <sub>2</sub> H] <sup>+</sup> · [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>
[1,2-en( $\eta^5$ -Ind) <sub>2</sub> ]TiMe <sub>2</sub>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>

Abbreviations: Me = methyl, Et = ethyl, Bu<sup>t</sup> = tert-butyl, Bu<sup>i</sup> = iso-butyl, Bz = benzyl, Pr<sup>i</sup> = 2,2-isopropylidene, Me<sub>2</sub>Si = dimethylsilylene, Ind = indenyl, THInd = 4,5,6,7-tetrahydroindenyl, Flu = fluorenyl, 1,2-en = 1,2-ethylidene, Ph<sub>2</sub>Si = diphenylsilylene, R<sup>6</sup> = (methyl, ethyl or isobutyl).

Also included in the scope of the present invention are those components (A) consisting of or obtained by starting from a metallocene belonging to any one of the groups previously described, which is supported on an inorganic or polymeric organic solid inert medium, preferably selected from inert inorganic oxides, more preferably selected from alumina, silica and silicoaluminates. These supported complexes can be obtained by impregnating the carrier with a solution in an inert solvent of the metal complex, or they can be prepared with methods which comprise the formation of relatively stable chemical bonds between complex and carrier. Supported ionic metallocene derivatives active in the polymerization of olefins without aluminoxanes or other organo-oxygenated compounds of non-transition metals, and methods for their preparation, are described in literature, for example, in published European patent application Nr. EP-A 522.581 and in International patent application WO 91/09882.

Component (B) of the catalyst of the present invention consists of a weakly co-ordinating, aprotic polar compound.

olefins wherein the component (A) as such is used as catalyst.

The catalysts of the present invention can be used in the (co)polymerization of olefins to give linear polymers having different characteristics as a function of the olefin(s) which is (co)polymerized and the process conditions. Alpha-olefins which can be polymerized with the catalysts of the present invention preferably contain from 2 to 20 carbon atoms and can also comprise heteroatoms. The present catalyst can preferably be used in homo- and co-polymerization processes of 1-alkenes such as ethylene, propylene, 1-butene, 4-methylpentene, 1-octene, 1-decene, styrene, etc., to give amorphous or crystalline polymers with a high molecular weight or also of a lower molecular weight, when desired, the polymerization being carried out under suitable conditions for the purpose, normally known in the art.

The catalysts of the present invention can be used with excellent results in the polymerization of ethylene to give linear polyethylene and in the copolymerization of ethylene with propylene or higher alpha-olefins to give copolymers having different characteristics depending on the specific polymerization conditions and the quantity and structure of the alpha-olefin itself used as comonomer. The catalyst of the present invention can also be conveniently used for the terpolymerization of ethylene, propylene and a diene to obtain vulcanizable rubbers of the EPDM type.

When the component (A) is suitably structured for the aim, the present catalysts can also be advantageously used for the stereoselective polymerization of alpha-olefins, preferably containing from 3 to 20 carbon atoms, to obtain iso- or syndiotactic polyolefins with a high stereospecificity. The iso- or syndio-tactic orientation essentially depends on the structure of the alpha-olefin which is polymerized. For example, isotactic polymers of propylene (isotactic polypropylene) and 1-butene (isotactic poly-1-butene) and syndiotactic polymers of styrene and its homologous substitutes, are obtained.

The catalysts of the present invention can be used with excellent results in essentially all known polymerization processes of alpha-olefins, and particularly in processes in suspension, at low, medium or high pressure and at temperatures of between 50 and 240°C, or in processes in solution in an inert diluent operating normally at pressures of between 10 and 150 bars and temperatures of between 50 and 230°C. Hydrogen is usually used as molecular weight regulator. Preferably the catalyst of the present invention is used in polymerization processes at temperatures comprised between 50 and 140 °C.

In all cases, the catalysts of the present invention are characterized by a notable increase in activity with respect to that which can be obtained with component (A) alone, without the addition of the weak co-ordinating polar compound (B). Increases in productivity even up to fifteen times greater than that of component (A) alone under the same conditions are surprisingly obtained with the improved catalysts of the present invention. Although not being bound to any particular theory, it is believed that the higher activity with respect to component (A) alone may derive both from an activating and stabilizing effect of component (B).

According to a particular aspect of the present invention, the improved catalyst for the (co)polymerization of alpha-olefins is prepared separately in accordance with one of the methods mentioned above, and subsequently introduced into the polymerization environment. The catalyst can be charged first into the polymerization reactor followed by the reagent mixture containing the alpha-olefin and possible comonomers, or the catalyst can be charged in the reactor already containing the reagent mixture, or, finally, the reagent mixture and the catalyst can be fed contemporaneously into a continuous reactor.

According to another aspect of the present invention, the catalyst is formed in situ in the polymerization reactor, for example by charging components (A) and (B) separately from each other in the appropriate proportions and possibly in the presence of an inert solvent.

According to the present invention, component (B) can also be fed to the reactor mixed with the stream containing the monomer, component (A) being fed separately.

The present invention is further described by the following examples which however are purely illustrative and do not limit the overall scope of the invention itself.

#### EXAMPLE 1

A solution of a catalyst of the present invention is prepared as follows:

0.46 ml of a 1.8 M solution of aluminium ethyldichloride in toluene ( $\text{AlEtCl}_2$ , 0.8 mmoles, commercial product ALDRICH) are added to a solution obtained by dissolving 25.8 mg of bis( $\eta^5$ -cyclopentadienyl)titanium dichloride (commercial product ALDRICH, 0.1 mmoles), purified by sublimation, in 15 ml of anhydrous toluene, and the mixture is left under stirring for 10 minutes at room temperature; a solution is obtained which is initially orange and subsequently darkens to brownish colour (component A).

0.6 ml of pentafluoroanisole (PFA, commercial product ALDRICH, 25 mmoles, component B) previously distilled on calcium hydride are then added and the mixture is left under stirring for a further 10 minutes at room temperature; an olive-green solution of the desired catalyst is obtained (molar ratios  $\text{Al/Ti/PFA}=8/1/40$ ), which is maintained under an inert atmosphere.

100 ml of toluene are charged into a 250 ml tailed test-tube in a nitrogen atmosphere, previously deaerated by vacuum/nitrogen repeated three times. The nitrogen is then substituted with ethylene (purity 99.95%), carrying out three

Example	Component (B)	Amount of (B) (mmoles)	Yield PE (g)	Activity [ $\frac{g_{PE}}{(mmole_{Zr} \cdot 100 \text{ kPa}_{(ethylene)} \cdot h)}$ ]
3	1,2,3,4,5-pentafluoroanisole (PFA)	12.5	6.7	838
4*	None	0.0	1.0	125
5	trifluoromethylphenylether	12.5	1.3	158
6	2,2,5,5-tetramethyltetrahydrofuran	12.5	1.7	207
7	1,3-dimethoxybenzene	12.5	2.0	244
8	4-fluoroanisole	26.0	3.0	366
9	Pentafluoropyridine	12.5	3.8	463
10*	Diisobutylphthalate	12.5	0.0	0
11*	Diisobutylphthalate	2.6	0.0	0
12*	Tetrahydrofuran	12.5	0.0	0

\* Comparative Example

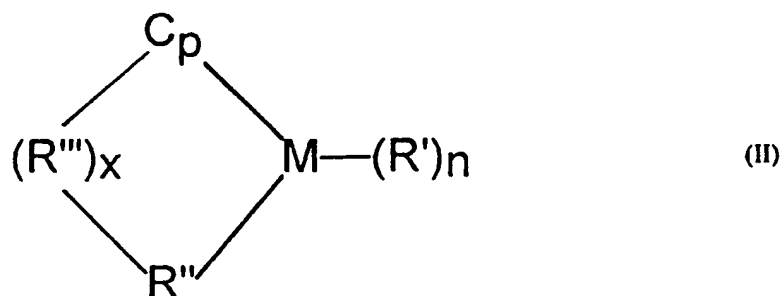
**TABLE 2: ethylene polymerization**

### EXAMPLE 13

A 1 liter autoclave, prepared and equipped as previously described in example 3, is filled with 470 ml of anhydrous toluene (distilled on metallic sodium) and 30 ml anhydrous 1-hexene. Ethylene is then introduced up to a pressure of 202 kPa (2 atm). The temperature is brought to 40°C. The autoclave is depressurized and 15.0 ml of the catalyst solution prepared according to previous example 3 are charged (0.023 mmole Zr), under ethylene flow. The pressure is brought again to 202 kPa, with the immediate start of the polymerization reaction which is carried out for 10 minutes maintaining the autoclave at 40°C under stirring, and continuously feeding ethylene to maintain the pressure constant at the initial preset value. At the end of the reaction, the polymer is recovered by precipitation with acidified methanol and subsequent washings with acetone.

After drying at room temperature in a stream of air, 1.2 g of ethylene/1-hexene copolymer are obtained with a cat-

2. The catalyst according to claim 1, wherein said metallocene derivative comprises or can be obtained starting from a metallocene having the following formula (II):



wherein:

M represents a metal selected from metals of groups 3 to 5, or from the group of lanthanides in the periodic table of elements;

Cp is an anion containing a  $\eta^5$ -cyclopentadienyl ring co-ordinated to the metal M;

each of the n R' independently represent a substituent group selected from hydride, halide, a C<sub>1</sub>-C<sub>8</sub> alkyl group, a C<sub>3</sub>-C<sub>12</sub> alkylsilyl group, a C<sub>5</sub>-C<sub>8</sub> cycloalkyl group, a C<sub>6</sub>-C<sub>10</sub> aryl group, a C<sub>1</sub>-C<sub>8</sub> alkoxy group, a C<sub>1</sub>-C<sub>8</sub> carboxyl group, a C<sub>2</sub>-C<sub>10</sub> dialkylamide group and a C<sub>4</sub>-C<sub>20</sub> alkylsilylamide group;

R'' represents a substituent group of the same nature as the previous R' groups, independently selected from these, or a second anion containing an  $\eta^5$ -cyclopentadienyl ring co-ordinated to the metal M;

R''' represents a divalent group having from 1 to 10 carbon atoms, optionally containing one or more heteroatoms, preferably O, N, P or Si, which is bridge-linked between Cp and R'' with a covalent bond. R''' is preferably selected from alkylene, dialkylsilylene, diarylsilylene, alkyl- or aryl amino or phosphino radicals, arylene, arylene-bis-alkylene etc.

"n" is an integer and is equal to the valence of M less 2;

"x" can be 0 or 1.

3. The catalyst according to claim 2, wherein, in formula (II), "x" is 1, R''' is selected from alkylene, dialkylsilylene, diarylsilylene, arylene and arylene-bis-alkylene and R'' is a second anion containing a  $\eta^5$ -cyclopentadienyl ring co-ordinated to the metal M.
4. The catalyst according to claim 2, wherein, in formula (II), "x" is 0, and R'' is a second anion containing a  $\eta^5$ -cyclopentadienyl ring co-ordinated to the metal M.
5. The catalyst according to any of the previous claims, wherein the metal of said metallocene derivative is selected in the group consisting of titanium, zirconium and hafnium.
6. The catalyst according to any of the previous claims, wherein said metallocene derivative is of an ionic nature and the metal M is included in the cation.
7. The catalyst according to any of the previous claims, wherein said metallocene derivative in component (A) is in solution or in suspension in an inert liquid medium, preferably apolar.
8. The catalyst according to any of the previous claims, wherein said metallocene derivative in component (A) is supported on an inert solid medium, preferably selected from inert inorganic oxides, more preferably selected from alumina, silica and silicoaluminates.
9. The catalyst according to any of the previous claims, wherein said component (B) consists of a compound having a dielectric constant greater than or equal to 3 and a co-ordinating capacity DN less than or equal to 10 kcal/mole.
10. The catalyst according to any of the previous claims, wherein said component (B) consists of a compound having a co-ordinating capacity DN less than or equal to 5.0 kcal/mole.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 96 11 6658

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL. 6)
D,X	DE 44 26 122 A (NIPPON OIL CO LTD) * claims; page 10, lines 52-66; page 15, example 5 *	1-11, 15-20	C08F10/02 C08F4/642
D,X	EP 0 648 786 A (TOSOH CORP) * claims; page 6, 37-45 *	1-9,11	
X	EP 0 644 206 A (SHOWA DENKO KK) * claims *	1	
D,A	EP 0 520 732 A (DOW CHEMICAL CO) * claims *	1-20	
			TECHNICAL FIELDS SEARCHED (Int. CL. 6)
			C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21 February 1997	Examiner Mergoni, M
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